行政院國家科學委員會補助專題研究計畫成果報告

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※ **含氮氧及硫雜環化合物光化學之研究** ※
※ Photochemistry on the Heterocyclics ※
※ with N, S and O ※
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計畫類別：個別型計畫
計畫編號：NSC　89－2113－M－002－010－
執行期間：88 **年** 08 **月** 01 **日至** 89 **年** 07 **月** 31 **日**

計畫主持人：台灣大學化學系　何東英

中文摘要:

研究苯乙烯呋喃，苯乙烯噻吩及苯乙烯派咯之烷基醚化合物之光化學反應。當此類化合物以二氯甲烷為溶劑進行光化學反應時，可得一種 5-(3-**酮**-1-**丁烯**) **苯**[b] **呋喃，噻吩及派咯等官能基之產物。當溶劑改為去水之苯時，則甲氧基醚為能完全水解而得到丁二烯醚之產物，此種與溶劑有關之光化學反應之反應機構包含了順反異構化作用，**[1,9]**氫位移，開環反應及丁二烯醚之水解作用。此種反應之產率高且產物單純，具有實用價值。**

關鍵詞：

苯乙烯雜環化合物，水解反應，光轉位反應。

Abstract：

Photolysis of alkyl- or aryl- 2-styrylfurans and 2-styrylthiophenes in dehydrated benzene affords 5-(3-RO-1, 3-butadienyl)benzo[b]furan, -thiophene in good yields. Photolysis of alkyl- or aryl-2-styrylfurans, 2-styrylthiophenes and 2-styryl-N-methylpyrrols in dichloromethane gives 5-(3-oxo-1-butenyl)benzo[b]furan, -thiophene and N-methyl-pyrrole respectively in good isolated yields.

Keywords:

Styrylheterocycles, Photorearrangement, Hydrolysis.

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□赴國外出差或研習心得報告一份

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□國際合作研究計畫國外研究報告書一份

執行單位：台灣大學化學系

中　華　民　國 89 **年**　10 **月**　31 **日**

行政院國家科學委員會專題研究計畫成果報告

含氮氧及硫雜環化合物光化學之研究
Photochemistry on the Heterocyclics with N, S and O

計畫編號：NSC 89－2113－M－002－010－
執行期限：88 **年** 08 **月** 01 **日至** 89 **年** 07 **月** 31 **日**
主持人：台灣大學化學系　何東英

一、中文摘要

研究苯乙烯呋喃，苯乙烯噻吩及苯乙烯派咯之烷基醚化合物之光化學反應。當此類化合物以二氯甲烷為溶劑進行光化學反應時，可得一種 5-(3-**酮**-1-**丁烯**) **苯**[b]**呋喃，噻吩及派咯等官能基之產物。當溶劑改為去水之苯時，則甲氧基醚為能完全水解而得到丁二烯醚之產物，此種與溶劑有關之光化學反應之反應機構包含了順反異構化作用，**[1,9] **氫位移，開環反應及丁二烯醚之水解作用。此種反應之產率高且產物單純，具有實用價值。**

關鍵詞：苯乙烯雜環化合物，水解反應，光轉位反應。

Abstract

Photolysis of alkyl- or aryl- 2-styrylfurans and 2-styrylthiophenes in dehydrated benzene affords 5-(3-RO-1, 3-butadienyl)benzo[b]furan, -thiophene in good yields. Photolysis of alkyl- or aryl-2-styrylfurans, 2-styrylthiophenes and 2-styryl-N-methylpyrrols in dichloromethane gives 5-(3-oxo-1-butenyl)benzo[b]-furan, -thiophene and N-methyl- pyrrole respec-tively in good isolated yields.

Keywords:

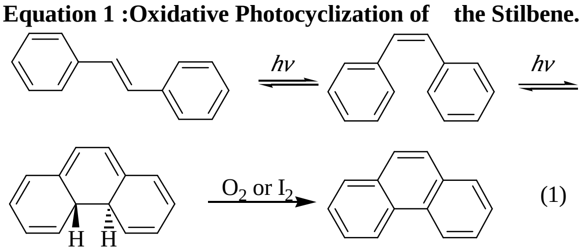
Styrylheterocycles, Photorearrangement, Hydrolysis.

Introduction

Rearrangement is one of the most important topics in photochemical reactions. It is especially important for reactions involving a complicated skeletal change that can provide abundant information for mechanistic considerations.(1) Solvent-dependent photochemical reactions have recently become a topic of interest.(2)-(4)

Stilbene and its derivatives are photochemically active.(5), (6) Under oxidative conditions, phenanthrene can be a major product through isomerization and oxidative photocyclization (Eq. 1).(7)

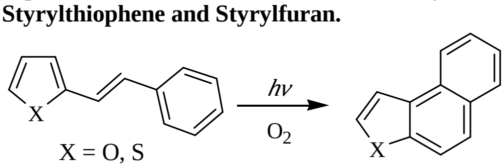
Equation 1 :Oxidative Photocyclization of the Stilbene.



(1)

Styrylthiophene(8) and styrylfuran(9) can also be transformed photochemically into the corresponding heterocycles through oxidative cyclization. (Eq. 2)

Equation 2 : Oxidative Photocyclization of Styrylthiophene and Styrylfuran.

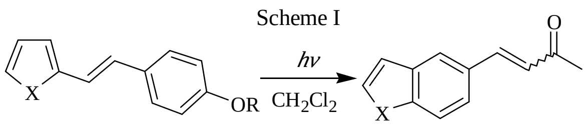


(2)

Results

Using the Wittig reaction,[10] we have prepared *p*-RO(R = alkyl or aryl)-2-styrylfurans (**1a-f**)[11], 2-styrylthiophenes (**2a-f**)[12] and 2-styryl-*N*-methyl-pyrrole (**3**)[13] (Scheme I) and report here novel solvent-dependent photochemical rearrangements for this series of styrylheterocycles.

Scheme I : Photochemical Rearrangements in CH_2Cl_2.



1 - 3 **4 - 6**

1a (X = O, R = Me), **2a** (X = S, R = Me), **3** (X = NMe, R = Me),
1b (X = O, R = Et), **2b** (X =S, R = Et), **4** (X = O),
1c (X = O, R = ^{n}Bu), **2c** (X = S, R= ^{n}Bu), **5** (X = S),
1d (X = O, R = Ph), **2d** (X = S, R = Ph), **6** (X = NMe),
1e (X = O, R = PhMe), **2e** (X = S, R = PhMe),
1f (X = O, R = Me (5-Me)), **2f** (X = S, R = 1-naphthyl).

Irradiation of a 1×10^{-2} M undehydrated solution (CH_2Cl_2) of *p*-methoxy-styrylfuran (**1a**) with a Rayonet reactor (350 nm) for 3 hours, gave 5-(3-oxo-1-butenyl)benzo[b]furan (**4**)[14] as the sole isolated product in 94% yield. The infrared spectrum indicated strong absorption at 1662 cm^{-1} and 1635 cm^{-1} for the conjugated carbonyl functional group. ^{1}H NMR ($CDCl_3$): δ 7.59(d, J = 16.1 Hz, 1H), 6.69(d, J = 16.1 Hz, 1H), 2.36(s, 3H) and ^{13}C NMR: δ 198.1 ppm are consistent with this structure. The products consist of two isomers. The major *E*-isomer can be isolated in large quantity. Similarly, irradiation of other ether derivatives (**1b-f**) in dichloromethane solution gave the corresponding benzo[b]furan (**4**) in high yields, and again the major products were the *E*-isomers. (Table 1) Irradiation of the starting material (**1a-f**) in dehydrated dichloromethane resulted in decreased yields of **4**.

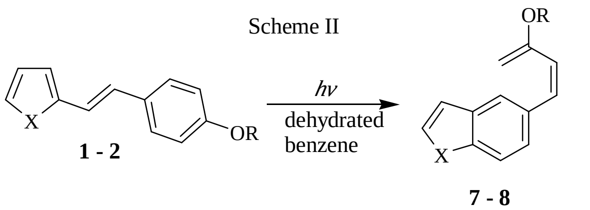
This novel photochemical rearrangement can also be applied to styrylthiophenes (**2a-f**)[15] and styryl-*N*-methylpyrrole (**3**)[16]. (Scheme I) The yields are also good for the styrylthiophenes, however more time is needed for photolysis (10 and 20 hours for styrylthiophenes and styrylpyrrole, respectively).

Table 1: Chemical Yields for the Photochemical Reactions of 1a-f, 2a-f and 3 at 350 nm in undehydrated dichloromethane solvent.

Reactants	Irrad. Times (hr)	Products	Conversions (%)	Yields (%)	*E/Z* ratio
1a	3	**4**	97	94	93/7
1b	3	**4**	97	96	100/0
1c	3	**4**	95	95	94/6
1d	3	**4**	80	93	100/0
1e	3	**4**	75	89	100/0
1f	4	**4**	97	90	93/7
2a	10	**5**	98	88	93/7
2b	10	**5**	91	90	88/12
2c	10	**5**	89	93	94/6
2d	10	**5**	98	98	97/3
2e	10	**5**	93	90	87/13
2f	10	**5**	97	96	96/4
3	20	**6**	51	75	100/0

In dehydrated benzene (or toluene), however, upon irradiation of a 1×10^{-2} M *p*-ethoxy- styrylthiophene (**2b**), the isolated compound shows ^{1}H NMR peaks at δ 7.39(d, J = 15.8 Hz, 1H), 6.62(d, J = 15.8 Hz, 1H), 4.28(d, J = 1.3 Hz, 1H), and 4.18(d, J = 1.3 Hz, 1H). Based on these results, the isolated product is considered to be 5-(3-ethoxy-1,3-butadienyl)-benzo-[b]thiophene (**8b**) (Scheme II). Similarly, upon irradiation of **1a**, **1b**, **1e**, **1f**, **2a**, and **2e** in dehydrated benzene, the photochemical products are the corresponding *Z*- and *E*-dienol ethers.[17] The yields are also good and a mixture of *E*- and *Z*-isomers is usually obtained. It is difficult to isolate the pure isomers. In some cases, we did isolate the pure *Z*-form. (Table 2) Further irradiation of the isolated pure *Z*-isomer or a *Z,E*-mixture of **7** or **8** in hydrated dichloromethane leads to the isolation of **4** or **5,** respectively. Thus, it is clear that the dienol ether compounds (**7**, **8**) are precursors of the 3-oxo-1-butenyl compounds (**4**, **5**). The decreased yields for **4** and **5** when **7** and **8** are photolyzed in hydrated benzene solution indicates that photochemical hydration is less efficient in hydrated benzene. No dienol ethers (**7**, **8**) are obtained upon photolysis of a dehydrated dichloromethane solution containing the starting material (**1**, **2**).

Scheme II : Photochemical Rearrangements in Dehydrated Benzene.



1a (X = O, R = Me), **7a** (X = O, R = Me),
1b (X = O, R = Et), **7b** (X = O, R = Et),
1e (X = O, R = PhMe), **7e** (X = O, R = PhMe),
1f (X = O, R = Me (5-Me)), **7f** (X = O, R = Me (2-Me)),
2a (X = S, R = Me), **8a** (X = S, R = Me),
2b (X = S, R = Et), **8b** (X = S, R = Et),
2e (X = S, R = PhMe). **8e** (X = S, R = PhMe).

Table 2: Chemical Yields for Photochemical Reactions of 1a, 1b, 1e, 2a, 2b, and 2e at 350 nm in dehydrated benzene

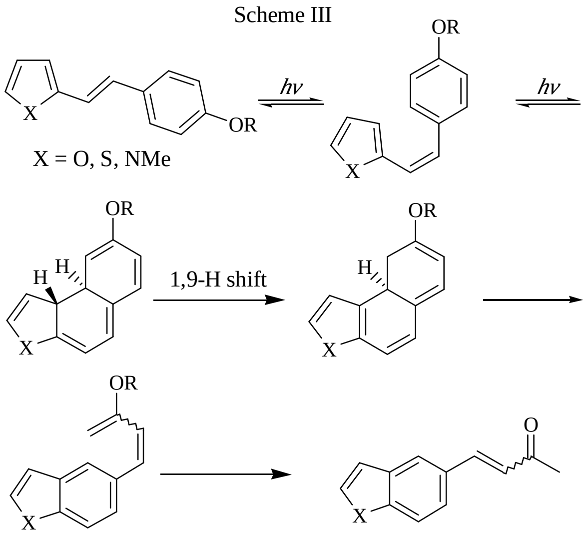
Reactants	Irrad. Times (hr)	Products	Conversions (%)	Yields (%)	*Z/E* ratio
1a	16	**7a**	90	87	54/46
1b	20	**7b**	68	82	80/20
1e	20	**7e**	58	74	68/32
2a	36	**8a**	68	72	68/32
2b	36	**8b**	78	77	92/8
2e	48	**8e**	58	64	61/39

Discussion

The mechanism for this novel photochemical rearrangement involves a photochemical conrotatory cyclization, a novel 1,9-hydrogen shift, lateral ring opening,[18] and finally photochemical conversion of the dienol ether to the conjugated ketone (Scheme III).

In conclusion, a novel solvent-dependent photochemical rearrangement reaction is reported for the alkoxy or aryloxy ethers of styrylfuran, styrylthiophene and styrylpyrrole. The reaction yields are high and the product is clean. These constitute novel synthetic routes for the transformation of styrylheterocycles to benzo-[b]heterocycles with a substituent which contains a dienyl ether or conjugated ketone functionality, which can be controlled by choosing a suitable solvent. The reaction mechanism of this novel rearrangement includes photochemical cyclization, 1,9-hydrogen shift, ring opening and photochemical transformation of dienol ether to conjugated ketone. The final step is very sensitive to the solvent and can occur efficiently in hydrated dichloromethane medium; if the solvent is less-polar dehydrated benzene, the hydration reaction dose not occur.

Scheme III : Mechanism of Photochemical Rearrangements



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(11) Spectral data for compound **1a**: mp 73.5 ~ 74°C; ^{1}H NMR(200 MHz, $CDCl_3$): δ 7.36–7.41(m, 3H), 6.99(d, *J* = 16.3 Hz, 1H), 6.86(d, *J* = 8.8 Hz, 2H), 6.75(d, *J* = 16.3 Hz, 1H), 6.39(dd, *J* = 1.9, 3.3 Hz, 1H), 6.28(d, *J* = 3.3 Hz, 1H), 3.79(s, 3H); ^{13}C NMR(50 MHz, $CDCl_3$): δ 159.3, 153.5, 141.7, 129.8, 127.5, 126.8, 114.6, 114.1, 111.5, 107.6, 55.3; MS(70 eV, EI): 186(M^+, 69), 185(42), 171(100), 143(43), 115(45).

(12) **2a**: mp 134 ~ 135°C; ^{1}H NMR(200 MHz, $CDCl_3$): δ 7.40(d, *J* = 8.8 Hz, 2H), 7.15(d, *J* = 5.4 Hz, 1H), 7.10(d, *J* = 16.1 Hz, 1H), 6.96–7.06(m, 2H), 6.90(d, *J* = 8.8 Hz, 2H), 6.88(d, *J* = 16.1 Hz, 1H), 3.81(s, 3H); ^{13}C NMR(50 MHz, $CDCl_3$): δ 159.2, 143.2, 129.7, 128.0, 127.5, 127.4, 125.3, 123.7, 119.7, 114.1, 55.2; MS(70 eV, EI): 216(M^+, 100), 201(36), 171(22), 129(32), 115(42).

(13) **3a**: ^{1}H NMR(200 MHz, $CDCl_3$): δ 7.38(d, *J* = 8.7 Hz, 2H), 6.87(d, *J* = 8.7 Hz, 2H), 6.82(s, 2H), 6.61(dd, *J* = 1.9, 4.3 Hz, 1H), 6.43(dd, *J* = 1.7, 3.7 Hz, 1H), 6.13(dd, *J* = 2.7, 3.7 Hz, 1H), 3.81(s, 3H), 3.67(s, 3H); ^{13}C NMR(50 MHz, $CDCl_3$): δ 130.1, 127.1, 126.9, 125.8, 123.1, 115.2, 114.1, 113.4, 108.1, 106.0, 55.3, 34.1; MS(70 eV, EI): 213(M^+, 9), 185(38), 126(100), 95(48), 83(72).

(14) 4-oxainden-5-yl-but-3-en-2-one(**4**): mp 74 ~ 75°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76(s, 1H), 7.65(d, *J* = 2.2 Hz, 1H), 7.62(d, *J* = 16.1 Hz, 1H), 7.50(d, *J* = 0.8 Hz, 2H), 6.78(d, *J* = 2.2 Hz, 1H), 6.72(d, *J* = 16.1 Hz, 1H), 2.36(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.1, 156.1, 146.0, 143.8, 129.4, 128.0, 126.0, 124.3, 121.8, 111.9, 106.7, 27.4; MS (70 eV, EI): 186(M^+, 87), 171(100), 143(44), 115(64); HR-MS: calcd. for $C_{12}H_{10}O_2$: 186.0681, found: 186.0683.

(15) 4-benzo[b]thiophen-5-yl-but-3-en-2-one(**5**): mp 101 ~ 102°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.94(d, *J* = 1.6 Hz, 1H), 7.86(d, *J* = 8.4 Hz, 1H), 7.62(d, *J* = 16.2 Hz, 1H), 7.52(dd, *J* = 1.6, 8.4 Hz, 1H), 7.47(d, *J* = 5.5 Hz, 1H), 7.34(dd, *J* = 0.6, 5.5 Hz, 1H), 6.77(d, *J* = 16.2 Hz, 1H), 2.39(s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 198.1, 143.6, 141.7, 139.9, 130.7, 127.6, 126.6, 124.3, 124.0, 123.1, 122.9, 27.5; MS (70 eV, EI): 202(M^+, 100), 187(88), 159(27), 115(51); HR-MS: calcd. for $C_{12}H_{10}OS$: 202.0452, found: 202.0451.

(16) 4-(1-methylindol-5-yl)but-3-en-2-one(**6**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78(s, 1H), 7.65(d, *J* = 16.2 Hz, 1H), 7.45(d, *J* = 8.7 Hz, 1H), 7.29(d, *J* = 8.7 Hz, 1H), 7.05(d, *J* = 3.0 Hz, 1H), 6.70(dd, *J* = 16.2 Hz, 1H), 6.57(d, *J* = 3.0 Hz, 1H), 3.77(s, 3H), 2.37(s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 198.5, 145.6, 137.9, 130.0, 128.7, 125.8, 124.4, 122.8, 121.1, 109.8, 102.0, 32.9, 27.4; MS (70 eV, EI): 199(M^+, 86), 184(100), 156(26), 141(19); HR-MS: calcd. for $C_{13}H_{13}ON$: 199.0997, found: 199.1004.

(17) 3-methoxy-1-oxaiden-5-yl-1,3-butadiene(*Z*-**7a**): ^{1}H NMR (300 MHz, C_6D_6): δ 7.55(s, 1H), 7.25(d, *J* = 8.6 Hz, 1H), 7.17(dd, *J* = 1.3, 8.6 Hz, 1H), 7.11(d, *J* = 2.1 Hz, 1H), 6.45(d, *J* = 12.5 Hz, 1H), 6.28(d, *J* = 2.1 Hz, 1H), 6.00(d, *J* = 12.5 Hz, 1H), 4.24(d, *J* = 2.0 Hz, 2H), 3.10(s, 3H); *E*-**7a**: ^{1}H NMR (300 MHz, C_6D_6): δ 7.41(s, 1H), 7.34(d, *J* = 15.9 Hz, 1H), 7.30(s, 2H), 7.10(d, *J* = 2.1 Hz, 1H), 6.56(d, *J* = 15.9 Hz, 1H), 6.32(d, *J* = 2.1 Hz, 1H), 4.14(d, *J* = 1.7 Hz, 1H), 4.05(d, *J* =1.7 Hz, 1H), 3.34(s, 3H); 3-ethoxy-1-oxaiden-5-yl-1,3-butadiene(*Z*-**7b)**: ^{1}H NMR (300 MHz, C_6D_6): δ 7.58(s, 1H), 7.30(s, 2H), 7.11(d, *J* = 2.2 Hz, 1H), 6.46(d, *J* = 12.5 Hz, 1H), 6.32(d, *J* = 2.2 Hz, 1H), 6.00(d, *J* = 12.5 Hz, 1H), 4.25(d, *J* = 1.4 Hz, 1H), 4.08(d, *J* = 1.2 Hz, 1H), 3.37(q, *J* = 7.1 Hz, 2H), 0.83(t, *J* = 7.1 Hz, 3H); 3-ethoxy-1-benzo[b]thiophen-5-yl-1,3-butadiene(*Z*-**8b**): ^{1}H NMR (200 MHz, C_6D_6): δ 7.54(d, *J* = 1.1 Hz, 1H), 7.45(d, *J* = 8.5 Hz, 1H), 7.37(d, *J* = 15.8 Hz, 1H), 7.22(dd, *J* = 1.5, 8.5 Hz, 1H), 6.90(s, 2H), 6.62(d, *J* = 15.8 Hz, 1H), 4.28(d, *J* = 1.3 Hz, 1H), 4.18(d, *J* = 1.3 Hz, 1H), 3.59(q, *J* = 6.9Hz, 2H),1.17(t, *J* = 6.9 Hz, 3H); ^{13}C NMR (50 MHz, C_6D_6): δ 159.1, 140.5, 133.7, 130.5, 129.3, 128.3, 126.8, 125.2, 124.2, 123.1, 122.7, 87.4, 62.9, 14.5; MS (70 eV, EI): 230(M^+, 100), 209(93), 201(74), 194(64), 185(57), 173(38); HR-MS: calcd. for $C_{14}H_{14}OS$: 230.0766, found: 230.0764.

(18) We have studied a similar reaction mechanism for the *p*-alkylstyrylfurans. Ho, T.-I.; Wu, J.-Y.; Wang, S.-L. *Angew. Chem. Int. Ed.* **1999** submitted.